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(54) **LITHIUM COBALT SYSTEM COMPLEX OXIDE, LITHIUM SECONDARY BATTERY POSITIVE ELECTRODE ACTIVE SUBSTANCE AND LITHIUM SECONDARY BATTERY**

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a lithium cobalt system complex oxide that has little drop of discharge voltage at the final stage of discharge and has excellent rate characteristics and has little deterioration of cycle characteristics even under repeated use at high voltage, when it is employed as a positive electrode active substance of a lithium secondary battery.

SOLUTION: The lithium cobalt system complex oxide is expressed by a formula, LixCo1-y-zZryMezO2-a. In the formula, Me shows a metal element or a transition metal element other than Co and Zr which has atomic number of 11 and more, x is $1.00<x<1.20$, y is $0<y\leq 0.01$, z is $0\leq z<0.1$, and a is $-0.1\leq a\leq 0.1$.

* NOTICES *

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]A lithium cobalt system multiple oxide with this invention useful as positive active material of a lithium secondary battery, The fall of the discharge voltage of the lithium secondary battery positive active material containing this and the discharge last stage is small, a rate characteristic (load characteristic) is excellent, and degradation of the cycle characteristic under high tension is related with few lithium secondary batteries.
[0002]
[Description of the Prior Art]In recent years, the rechargeable lithium-ion battery is put in practical use as a power supply of sized electronic equipment, such as a laptop PC, a cellular phone, and a video camera, as portable-izing and cordless making progress quickly in homeuse electronics. About this rechargeable lithium-ion battery, the report ("material research bulletin" vol15, P783-789 (1980)) that cobalt acid lithium is useful as positive active material of a rechargeable lithium-ion battery is made by Hitoshi Mizushima 1980, and Since, The research and development about a lithium system multiple oxide are furthered actively, and the proposal of the former many is made.
[0003]In a rechargeable lithium-ion battery, as art of attaining high-energy-density-ization of positive active material, conventionally, The presentation of cobalt acid lithium For example, Li_xCoO_2. being referred to as (1.05<=x<=1.3 [however,]) -- lithium -- what was made rich (JP,3-127454,A). conversely, the thing to consider as Li_xCoO_2 (however, 0< x<=1) -- cobalt -- what was made rich (JP,3-134969,A). the thing (JP,3-201368,A.) which made metal ions, such as Mn, W, nickel, and La, dope JP,4-328277,A, JP,4-319259,A, etc., What makes remains Li_2CO_3 in cobalt acid lithium 10 or less % of the weight (JP,4-56064,A),What (JP,2000-12022,A) is expressed with Li_xCoO_2 (however, 0< x<=1.25), and carries out spin concentration

in g= 2.15 by an electron spin resonance apparatus in below a $1x10^{18}$ individual / g is proposed.
[0004]As what makes particle diameter requirements as a physical feature of cobalt-acid-lithium system positive active material, For example, the thing whose mean particle diameter of $LiCoO_2$ is 10-150 micrometers (JP,1-304664,A), That whose mean particle diameter of a primary particle is 0.5 micrometer or less (JP,4-33260,A), In mean particle diameter, 2-10 micrometers and the particle size distribution D (25%) 0.5-10 micrometers, That whose D (75%) D (50%) is 2-10 micrometers, and is 3.5-30 micrometers (JP,5-94822,A), In accumulation particle diameter, 3-15 micrometers and accumulation particle diameter 50% 10% 8-35 micrometers, what is the particle size distribution whose 90% accumulation particle diameter is 30-80 micrometers (JP,5-151998,A), and thing (JP,6-243897,A) 2-9 micrometers and whose 1 of them-9 micrometers mean particle diameter is not less than 60% of whole products etc. -- it is proposed.
[0005]However, the lithium secondary battery using the lithium cobalt system multiple oxide by which the conventional proposal is made as positive active material has the large fall of the discharge voltage of the discharge last stage, a rate characteristic is bad, and if charge and discharge are repeated under high tension, a cycle characteristic will deteriorate.
[0006]Then, the nonaqueous secondary battery which uses as positive active material the cobalt acid lithium which added the zirconium compound by the manufacturing stage of cobalt acid lithium is proposed in order to improve these characteristics. For example, some cobalt in cobalt acid lithium or this compound. The nonaqueous secondary battery using the positive active material which added the zirconium with 1 to 10% of compounding ratio by the mole ratio to cobalt to the multiple oxide replaced with the transition metal (JP,4-319260,A), General formula; The nonaqueous secondary battery using the cobalt acid lithium expressed with $Li_xCoZr_yO_z$ (0.01<=y<=0.30 and z are 1.95<=x<=3.00 in the inside of a formula, and x, as for 0.35<=x<=1.70 and y) as positive active material (JP,5-67467,A), General formula; the nonaqueous secondary battery (JP,7-235293,A) using the cobalt acid lithium which appears in $LiCo_xZr_yO_z$ (the inside of a formula, 0.9<=x<=1.0, 0< y<=0.1, 1.9<=z<=2.1) as positive active material etc. are proposed.
[0007]
[Problem(s) to be Solved by the Invention]However, the lithium cobalt system multiple oxide which added the zirconium atom indicated to JP,4-319260,A or JP,7-235293,A, In order to raise the cycle characteristic at the sacrifice of the service capacity of that whose cycle characteristic improves somewhat, there was a problem that service capacity was low. The lithium secondary battery using the lithium cobalt system multiple oxide indicated to JP,5-67467,A as positive active material, Although the cycle characteristic improved somewhat for

this reason, there was a problem that it was difficult to reduce initial service capacity substantially, therefore to secure capacity sufficient at the time of a heavy load.
[0008]Therefore, when the purpose of this invention is used as positive active material of a lithium secondary battery, Even if the fall of the discharge voltage of the discharge last stage is small, a rate characteristic is excellent and it repeats charge and discharge under high tension, providing the lithium secondary battery using few lithium cobalt system multiple oxides, the positive active material containing this, and this positive active material has degradation of a cycle characteristic.
[0009]
[Means for Solving the Problem]As a result of this invention person's inquiring wholeheartedly, in this actual condition the above-mentioned problem, Knowledge of being what is depended on Zr not being replaced by homogeneity and optimum dose in a lithium cobalt system multiple oxide like ZrO_2 separating on the surface of a lithium cobalt system multiple oxide with a lithium cobalt system multiple oxide, and existing in it was acquired. Based on this knowledge, and a lithium compound and a cobalt compound, When calcinating a zirconium compound and a mixture which contains a compound of a with an atomic numbers [other than Co and Zr] of 11 or more metallic element, or the transition metal element Me further as occasion demands and obtaining a lithium cobalt system multiple oxide, If Li, Co, Zr, etc. to which reaction raw materials other than a lithium compound and a lithium compound can react a mixture of a raw material enough should be made into quantity in a specific range as a raw material, using a reactant good zirconium compound, A part of Co is uniformly replaced by zirconium atom, without ZrO_2 with an unreacted lithium cobalt system multiple oxide obtained, etc. existing substantially, General formula $Li_xCo_{1-y-z}Zr_yMe_zO_{2-a}$ (among a formula) Me(s) are with an atomic numbers of 11 or more metallic elements or transition metal elements other than Co and Zr, x takes 1.00< x<1.20, y takes 0< y<=0.01, and z takes 0<=z<0.1 and a value of a-0.1<=a<=0.1. If it becomes what is expressed and this is used as positive active material of a lithium secondary battery, Fall of discharge voltage of the discharge last stage of a lithium secondary battery is small, and it excels in a rate characteristic, Even if it repeats charge and discharge under high tension, it finds out that degradation of a cycle characteristic decreases, and it came to complete this invention.
[0010]That is, this invention is a following general formula (1).;
$Li_xCo_{1-y-z}Zr_yMe_zO_{2-a}$ (1)
(Among a formula, Me(s) are with an atomic numbers of 11 or more metallic elements or transition metal elements other than Co and Zr, and) x takes 1.00< x<1.20, y takes 0< y<=0.01, and z takes 0<=z<0.1 and a value of a-0.1<=a<=0.1. A lithium cobalt system multiple oxide characterized by what is expressed is provided.

[0011]Lithium secondary battery positive active material, wherein this invention contains said lithium cobalt system multiple oxide is provided.
[0012]This invention provides a lithium secondary battery using said lithium secondary battery positive active material.
[0013]
[Embodiment of the Invention]The lithium cobalt system multiple oxide concerning this invention is expressed with the above-mentioned general formula (1). Among a formula (1), Me (s) are with an atomic numbers of 11 or more metallic elements or transition metal elements other than Co and Zr, and are replaced by the site which it is added by necessity in the lithium cobalt system multiple oxide expressed with the above-mentioned general formula (1), and Co occupies. It contains, in order that Me may improve the safety and cycle characteristic of a cell over a burst, liquid leakage, etc. of a cell in the lithium cobalt system multiple oxide concerning this invention. As such Me, for example, magnesium, aluminum, titanium, vanadium, chromium, iron, copper, zinc, yttrium, molybdenum, niobium, etc. are mentioned, and in this, since aluminum or niobium has the high safe performance of the above-mentioned cell, it is desirable. in this invention -- Me -- one of sorts of these -- or two or more sorts can be combined and it can use.
[0014]in the above-mentioned general formula (1), x shows the rate of Li in a lithium cobalt system multiple oxide -- usually -- $1.00< x<1.20$ -- it is $1.00< x<=1.10$ preferably.
[0015]moreover -- in the above-mentioned general formula (1), y shows the rate of Zr in a lithium cobalt system multiple oxide -- usually -- $0< y<=0.01$ -- it is $0.001<=y<=0.05$ preferably. If y is in this within the limits, even if the lithium secondary battery which uses this lithium cobalt system multiple oxide as positive active material has the small fall of the discharge voltage of the discharge last stage, and a rate characteristic is excellent and it repeats charge and discharge under high tension, degradation of a cycle characteristic will serve as few lithium secondary batteries. Making the lower limit of y into a larger value than 0, When a lithium cobalt system multiple oxide contains Zr of ultralow volume, it is for battery capacity, such as suppressing the fall of the discharge voltage of the discharge last stage, to improve by leaps and bounds compared with what does not contain Zr, or the thing which y contains exceeding 0.01, without reducing service capacity.
[0016]moreover -- in the above-mentioned general formula (1), z shows the rate of Me in a lithium cobalt system multiple oxide -- usually -- $0<=z<0.1$ -- it is $0<=z<0.05$ preferably. When z is in this within the limits, since battery characteristics, such as safety and a cycle characteristic, are improvable, it is desirable.
[0017]The lithium cobalt system multiple oxide expressed with the above-mentioned general formula (1) has alpha-$NaFeO_2$ mold structure. That is, the lithium cobalt system multiple oxide expressed with the above-mentioned general formula (1) is equivalent to that by which Me is

arranged by Li or necessity and Me is arranged by Co, Zr, Li, or necessity at the site of Na at the site of Fe in alpha-$NaFeO_2$ mold structure.

[0018]1-15 micrometers of mean particle diameter asked for the lithium cobalt system multiple oxide concerning this invention by the laser method are 1-20 micrometers usually 2-10 micrometers especially preferably preferably. When mean particle diameter is in this within the limits, since formation of the coat of uniform thickness is attained, it is desirable. The lithium cobalt system multiple oxide concerning this invention, In case of the primary particle aggregate with a mean particle diameter of 1.0-20 micrometers in which primary particles with a mean particle diameter of 0.1-2.5 micrometers gather further in addition to mean particle diameter being a thing in the above-mentioned specific range, Since the ejection and insertion of Li are promptly performed when using a lithium cobalt system multiple oxide as positive active material, it is desirable. Since [of a whole product] forming of the coat of uniform thickness becomes being 1-20 micrometers in particle diameter not less than 80% of preferably possible not less than 70%, the above-mentioned primary aggregate is more desirable. the lithium cobalt system multiple oxide concerning this invention -- a BET specific surface area -- usually -- $0.1\text{-}2m^2/g$ -- desirable -- $0.2\text{-}1.5m^2/g$ -- it is $0.3\text{-}1.0m^2/g$ especially preferably. When a BET specific surface area is in this within the limits, since safety is good, it is desirable.

[0019]Next, the manufacturing method of the above-mentioned lithium cobalt system multiple oxide is explained. As a manufacturing method of the above-mentioned lithium cobalt system multiple oxide, For example, a lithium compound, a cobalt compound, and a zirconium compound, It is a manufacturing method of the lithium cobalt system multiple oxide expressed with the above-mentioned general formula (1) which calcinates the mixture which contains the compound of a with an atomic numbers [other than Co and Zr] of 11 or more metallic element, or the transition metal element Me further as occasion demands, A reactant high thing is used as said zirconium compound, The method of carrying out mole-ratio M_{Zr}/M_{Co} of Zr to mole-ratio $M_{Li}/(M_{Co}+M_{Zr}+M_{Me})$ of Li to the number of sum total mols of Co, and Zr and Me and the number of mols of Co into a specific range in said mixture is mentioned.

[0020]In the manufacturing method of the above-mentioned lithium cobalt system multiple oxide, a lithium compound, a cobalt compound, a zirconium compound, and the mixture that contains the compound of a with an atomic numbers [other than Co and Zr] of 11 or more metallic element or the transition metal element Me further as occasion demands are prepared first.

[0021]As a compound of a with an atomic numbers [other than Co added / the lithium compound and cobalt compound which are used by carrying out a raw material, or if needed / for a mixture, and Zr] of 11 or more metallic element, or the transition metal element Me, If it

can obtain industrially, there will be no limitation in particular, for example, the oxide, hydroxide, carbonate, the nitrate, and organic acid salt of each metal will be mentioned. As a cobalt compound, since it is cheap, specifically, cobalt carbonate and cobalt oxide are [that it is easy to receive industrially] preferred. As a lithium compound, lithium carbonate is easy to come to hand industrially, and since it is cheap, it is preferred.

[0022]The inorganic zirconium compound where a reactant high zirconium compound is used as a zirconium compound for example, which has mean particle diameter in a specific range, or an organic zirconium compound is mentioned. As an inorganic zirconium compound, for example Zirconium hydride, zirconium hydroxide, Zirconium oxide, zirconium nitrate, carbonic acid zirconyl, phosphoric acid zirconyl, zirconium sulfate, carbonic acid zirconyl ammonium, etc. are mentioned, among these since it is cheap, zirconium oxide is [that it is easy to receive industrially] preferred.

[0023]As an organic zirconium compound, for example Acetic acid zirconyl, Stearic acid zirconyl, a caprylic acid zirconium, an oleic acid zirconium, A zirconiumtetramethoxide, zirconiumtetraethoxide, zirconium tetra-n-propoxide, Zirconium tetra-iso-propoxide, zirconium tetra-n-butoxide, Zirconium tetra-iso-butoxide, zirconium tetra-sec-butoxide, Zirconium tetra-tert-butoxide, zirconium acetylacetone tributoxide, Rather than the organic compound of a zirconyl system which zirconium acetylacetonato etc. are mentioned and is expressed with general formula;$ZrO(R)_2$ (an organic group is shown in the inside R of a formula.) in this. General formula; since [desirable and] the organic compound of reactivity of the zirconium system expressed with $Zr(R)_4$ (an organic group is shown in the inside R of a formula.) is especially better, and it is industrially available, zirconium acetylacetonato is still more preferred.

[0024]0.1-5 micrometers of mean particle diameter asked for an inorganic zirconium compound by the laser method are usually 0.5-2 micrometers preferably. Since there is a possibility that condensation according that this mean particle diameter is less than 0.1 micrometer to electrostatic or moisture absorption may not fully be mixed, and Co may not fully be replaced, it is not desirable. If mean particle diameter exceeds 5 micrometers, ZrO_2 will not remain in the lithium cobalt system multiple oxide after calcination, substitution of Zr to Co site will no longer be performed uniformly, or impurities, such as Li_2ZrO_3, will be generated, Since battery capacity becomes low like the service capacity per weight falling and a rate characteristic and a cycle characteristic not being improved when it is considered as the positive active material of a lithium secondary battery, it is not desirable.

[0025]With ZrO_2 which remains in the lithium cobalt system multiple oxide after calcination. ZrO_2 unreacted when ZrO_2 is used as a zirconium compound remains as it is, When zirconium

compounds other than ZrO_2 are used as a zirconium compound, and manufacturing the lithium cobalt system multiple oxide expressed with the above-mentioned general formula (1), ZrO_2 which carries out a byproduction remains.

[0026]Since reactivity is high compared with an inorganic zirconium compound, it is not limited in particular for particle diameter, but since the direction of a detailed thing has higher reactivity, an organic zirconium compound is preferred. Specifically, the mean particle diameter of an organic zirconium compound is usually 0.5-10 micrometers preferably 0.1-20 micrometers. It is.

[0027]The compound of a with an atomic numbers [other than Co added by the above-mentioned cobalt compound, a lithium compound, a zirconium compound, and necessity and Zr] of 11 or more metallic element, or the transition metal element Me, Although neither asks a production history, in order to manufacture the lithium cobalt system multiple oxide of a high grade, it is preferred that there are few impurity contents as much as possible. the compound of a with an atomic numbers [other than Co added by the above-mentioned cobalt compound, a lithium compound, a zirconium compound, and necessity and Zr] of 11 or more metallic element, or the transition metal element Me -- respectively -- one sort -- or two or more sorts can be combined and it can use.

[0028]The compound of a with an atomic numbers [other than Co added as a preparing method of the above-mentioned mixture the above-mentioned lithium compound, a cobalt compound, or if needed and Zr] of 11 or more metallic element or the transition metal element Me is mixed by dry type or a wet type. Among these, since manufacture is easy, dry blending is preferred. In the case of dry blending, it is preferred to use a blender which a raw material mixes uniformly.

[0029]In the above-mentioned mixture, mole-ratio $M_{Li}/(M_{Co}+M_{Zr}+M_{Me})$ of Li to the number of sum total mols of Co, and Zr and Me, usually, $1<M_{Li}/(M_{Co}+M_{Zr}+M_{Me})$ -- it is preferably referred to as $1<M_{Li}/(M_{Co}+M_{Zr}+M_{Me})<1.2$. Here, M_{Li}, M_{Co}, M_{Zr}, and M_{Me} are the numbers of mols of Li, Co, Zr, and Me, respectively. Since Me is an optional component in the lithium cobalt system multiple oxide concerning this invention, when the compound of Me is not contained in the above-mentioned mixture, M_{Me} of $M_{Li}/(M_{Co}+M_{Zr}+M_{Me})$ is 0. As for $M_{Li}/(M_{Co}+M_{Zr}+M_{Me})$, when M_{Me} is 0, being referred to as $1<M_{Li}/(M_{Co}+M_{Zr}+M_{Me})<1.05$ is preferred. If $M_{Li}/(M_{Co}+M_{Zr}+M_{Me})$ is less than one in the above-mentioned mixture, Since the absolute magnitude of sufficient source of Li for making Me atom added Co atom, Zr atom, or if needed react runs short, the oxide of Co atom, Zr atom, or Me atom remains as a result and battery capacity, especially service capacity fall, it is not desirable.

[0030]mole-ratio M_{Zr}/M_{Co} of Zr [on the above-mentioned mixture and as opposed to the number of mols of Co] -- usually -- $0<M_{Zr}/M_{Co}<0.01125$ -- it is preferably referred to as $0.001<M_{Zr}/M_{Co}<0.005$. Since ZrO_2 remains that M_{Zr}/M_{Co} is 0.01125 or more in the lithium cobalt system multiple oxide after calcination and the above-mentioned battery capacity, especially service capacity fall remarkably, it is not desirable.
[0031]Next, a mixture is calcinated. The calcination temperature and firing time which can manufacture the lithium cobalt system multiple oxide expressed with the above-mentioned general formula (1) as a firing condition, and a zirconium compound does not remain or a by-product does not generate after calcination are chosen suitably. As a concrete firing condition, in using an organic zirconium compound as a raw material, What is necessary is for 600-1100 ** of calcination temperature to be usually 700-1000 ** preferably, and just to usually make firing time into 5 to 8 hours preferably for 3 to 10 hours, since the melting point is low and reactivity is generally good compared with an inorganic zirconium compound. In using an inorganic zirconium compound as a raw material, calcination temperature shall be 800-1050 ** preferably, and 600-1100 ** of firing time usually makes it 2 to 24 hours. Atmosphere of calcination may be performed by any in the atmosphere, oxygen environment, or an inert atmosphere, and is not restricted in particular, for example. The above-mentioned calcination can be performed any number of times as occasion demands.
[0032]After calcination cools fired material suitably and obtains the lithium cobalt system multiple oxide which grinds if needed and is applied to this invention. Grinding is suitably performed, when the lithium cobalt system multiple oxide produced by calcinating is a thing of the easily united block like shape, but the particle of a lithium cobalt system multiple oxide itself has the above-mentioned specific mean particle diameter and a BET specific surface area also before grinding. Since ZrO_2 does not remain in the form separated with the lithium cobalt system multiple oxide, the discharge last stage also has the small fall of discharge voltage, and the lithium cobalt system multiple oxide concerning this invention excels [last stage] in a rate characteristic and a cycle characteristic.
[0033]In the lithium cobalt system multiple oxide containing the conventional zirconium atom, even if it added the zirconium, existed in many cases, without ZrO_2 and Li_2ZrO_3 dissolving, and, for this reason, there was a problem that the service capacity itself fell, but. In the lithium cobalt system multiple oxide concerning this invention, since Zr has replaced by Co site in a lithium cobalt system multiple oxide uniformly and neither ZrO_2 nor Li_2ZrO_3 exists substantially, it becomes the thing excellent in battery capacities, such as the above-mentioned rate characteristic.
[0034]The lithium cobalt system multiple oxide concerning this invention can be conveniently

used as positive active material of the lithium secondary battery which consists of an anode, a negative electrode, a separator, and nonaqueous electrolyte containing lithium salt, for example.

[0035]The lithium secondary battery positive active material concerning this invention contains the above-mentioned lithium cobalt system multiple oxide. Positive active material is the positive electrode mixture of the below-mentioned lithium secondary battery, i.e., positive active material, a conducting agent, a binder, and one raw material of the mixture which consists of fillers etc. if needed. Since the lithium secondary battery positive active material concerning this invention contains the above-mentioned lithium cobalt system multiple oxide, when mixing with other raw materials and preparing positive electrode mixture, kneading is easy and the coating nature at the time of applying the obtained positive electrode mixture to a positive pole collector becomes easy.

[0036]The above-mentioned lithium secondary battery positive active material is used for the lithium secondary battery concerning this invention, and it consists of an anode, a negative electrode, a separator, and nonaqueous electrolyte containing lithium salt. For example spreading desiccation etc. carry out positive electrode mixture, an anode is formed on a positive pole collector, and positive electrode mixture consists of positive active material, a conducting agent, a binder, a filler added by necessity, etc. As for the lithium secondary battery concerning this invention, the aforementioned lithium cobalt system multiple oxide which is positive active material is uniformly applied to the anode. For this reason, neither the fall of the discharge voltage of the discharge last stage nor the fall of a rate characteristic and a cycle characteristic produces the lithium secondary battery concerning this invention easily.

[0037]Especially if it is an electronic conductor which does not cause a chemical change in the constituted cell as a positive pole collector, are not restricted, but. For example, that etc. to which the surface treatment of carbon, nickel, titanium, and the silver was carried out are mentioned to the surface of stainless steel, nickel, aluminum, titanium, baked carbon, aluminum, or stainless steel.

[0038]If it is a charge of an electronic conduction material which does not cause a chemical change in the constituted cell as a conducting agent, there will be no limitation in particular. For example, black lead, such as natural graphite and an artificial graphite, carbon black, acetylene black, Conductive materials, such as Ketchen black, carbon fiber and metal, nickel powder, a metal fiber, or a polyphenylene derivative, are mentioned, and flaky graphite, scaly graphite, earthy graphite, etc. are mentioned as natural graphite, for example. these -- one sort -- or two or more sorts can be combined and it can use. The rate of a compounding ratio of a conducting agent is 2 to 30 % of the weight preferably one to 50% of the weight among positive electrode mixture.

[0039]As a binder, for example Starch, polyvinylidene fluoride, polyvinyl alcohol,

Carboxymethyl cellulose, hydroxypropylcellulose, regenerated cellulose, Diacetyl cellulose, a polyvinyl pyrrolidone, tetra FUROORO ethylene, Polyethylene, polypropylene, an ethylene-propylene-diene terpolymer (EPDM), the polymer etc. which have polysaccharide, such as sulfonation EPDM, styrene butadiene rubber, fluorocarbon rubber, and polyethylene oxide, thermoplastics, and rubber elasticity are mentioned -- these -- one sort -- or two or more sorts can be combined and it can use. When using the compound containing a functional group which reacts to lithium like polysaccharide, it is preferred to, add a compound like an isocyanate group for example, and to deactivate the functional group. The rate of a compounding ratio of a binder is 5 to 15 % of the weight preferably one to 50% of the weight among positive electrode mixture.

[0040]A filler controls the cubical expansion of an anode, etc. in positive electrode mixture, and is added by necessity. If it is the fibrous material which does not cause a chemical change in the constituted cell as a filler, anything can be used, but textiles, such as olefin system polymer, such as polypropylene and polyethylene, glass, and carbon, are used, for example. Although the addition in particular of a filler is not limited, 0 to 30 % of the weight is preferred among positive electrode mixture.

[0041]On a negative pole collector, spreading desiccation etc. carry out a negative pole material, and a negative electrode is formed. Although in particular that is not restricted by the electronic conductor which does not cause a chemical change in the constituted cell as a negative pole collector, For example, the thing to which the surface treatment of carbon, nickel, titanium, and the silver was carried out, an aluminum cadmium alloy, etc. are mentioned to the surface of stainless steel, nickel, copper, titanium, aluminum, baked carbon, copper, or stainless steel.

[0042]Especially as a negative pole material, although not restricted, a carbonaceous material, a metal multiple oxide, a lithium metal, a lithium alloy, a silicon system alloy, a tin system alloy, a metallic oxide, a conductive polymer, a charcogen compound, Li-Co-nickel system material, etc. are mentioned, for example. As a carbonaceous material, the charge of a difficulty graphitized carbon material, a black lead system carbon material, etc. are mentioned, for example. As a metal multiple oxide, it is $Sn_pM^1{}_{1-p}M^2{}_qO_r$ (among a formula), for example. M^1 shows one or more sorts of elements chosen from Mn, Fe, Pb, and germanium, M^2 shows one or more sorts of elements chosen from aluminum, B, P, Si, the 1st fellows of the periodic table, the 2nd fellows, the 3rd fellows, and a halogen, 0< p<=1, 1<=q<=3, and 1<=r<=8 are shown. Compounds, such as $Li_xFe_2O_3$ (0<=x<=1) and Li_xWO_2 (0<=x<=1), are mentioned. As a metallic oxide, GeO, GeO_2, SnO, SnO_2, PbO, PbO_2, Pb_2O_3, Pb_3O_4, Sb_2O_3, Sb_2O_4, Sb_2O_5, Bi_2O_3, Bi_2O_4, Bi_2O_5, etc. are mentioned. Polyacethylene, Polly p-phenylene, etc. are

mentioned as a conductive polymer.

[0043]The insulating thin film which had the big degree of ion permeation as a separator, and had a predetermined mechanical strength is used. The sheet and nonwoven fabric which were built from organic solvent-proof nature and hydrophobicity from olefin system polymer, glass fiber, or polyethylene, such as polypropylene, etc. are used. As an aperture of a separator, generally what is necessary is just a range useful as an object for cells, and it is 0.01-10 micrometers. What is necessary is just to be in within the limits for common cells as thickness of SEPARETA, and it is 5-300 micrometers. A solid electrolyte seems to serve as a separator, when solid electrolytes, such as polymer, are used as an electrolyte mentioned later.

[0044]The nonaqueous electrolyte containing lithium salt consists of nonaqueous electrolyte and lithium salt. As nonaqueous electrolyte, nonaqueous electrolyte, an organic solid electrolyte, and an inorganic solid electrolyte are used. As nonaqueous electrolyte, for example N-methyl-2-pyrrolidinone, propylene carbonate, Ethylene carbonate, butylene carbonate, dimethyl carbonate, Diethyl carbonate, gamma-butyrolactone, 1, 2-dimethoxyethane, A tetrahydroxyfranc, 2-methyltetrahydrofuran, dimethyl sulfoxide, 1,3-dioxolane, a formamide, dimethylformamide, dioxolane, Acetonitrile, nitromethane, methyl formate, methyl acetate, trialkyl phosphate, Trimethoxy methane, a dioxolane derivative, sulfolane, 3-methyl-2-oxazolidinone, It is one sort of aprotic organic solvents, such as a propylene carbonate derivative, a tetrahydrofuran derivative, diethylether, 1,3-propane Salton, methyl propionate, and ethyl propionate, or the solvent which mixed two or more sorts is mentioned.

[0045]The polymer which contains a polyethylene derivative, a polyethylene oxide derivative, or this as an organic solid electrolyte, for example, The mixture etc. of polymer and phosphoric ester polymer containing a polypropylene oxide derivative or this, polymer containing an ionicity dissociable group, polymer containing an ionicity dissociable group, and the above-mentioned nonaqueous electrolyte are mentioned.

[0046]As an inorganic solid electrolyte, Li_3N, LiI, Li_5NI_2, and Li_3N-LiI-LiOH, $LiSiO_4$, and $LiSiO_4$-LiI-LiOH, Li_2SiS_3, a phosphorus sulfide compound, etc. are mentioned.

[0047]As lithium salt, what is dissolved in the above-mentioned nonaqueous electrolyte is used. For example, LiCl, LiBr, LiI, $LiClO_4$, $LiBF_6$, $LiPF_6$, $LiCF_3SO_3$, $LiCF_3CO_2$, $LiAsF_6$, $LiSbF_6$, $LiB_{10}Cl_{10}$, It is one sort, such as $LiAlCl_4$ and CH_3SO_3Li, CF_3SO_3Li, $(CF_3SO_2)2NLi$, chloroboranelithium, low-grade aliphatic-carboxylic-acid lithium, and 4 phenyl lithium borate, or the salt which mixed two or more sorts is mentioned.

[0048]To nonaqueous electrolyte, the compound shown below can be added in order to improve discharge, a charging characteristic, and fire retardancy. For example, pyridine, triethyl phosphite, triethanolamine, Cyclic ether, ethylenediamine, n-glyme, hexalin acid TORIAMIDO, Nitrobenzene derivative, sulfur, quinonimine dye, N-substitution oxazolidinone,

N, and N-substitution imidazolidine, Ethylene glycol dialkyl ether, ammonium salt, polyethylene glucohol, Pyrrole, 2-methoxyethanol, aluminum trichloride, the monomer of a conductive polymer electrode active material, Triethylene phosphonic amide, trialkylphosphine, morpholine, An aryl compound and hexamethylphosphoric triamide with a carbonyl group, 4-alkyl morpholine and the bicyclic third class amine, oil, phosphonium salt and the third class sulfonium salt, phosphazene, carbonic ester, etc. are mentioned. As shape of the lithium secondary battery concerning this invention, they may be which shape, such as a button, a sheet, a cylinder, an angle, and a coin type, for example.

[0049]The lithium secondary battery using $LiCoO_2$ is discharged by insertion of Li to the inside of the layer structure of a $LiCoO_2$ crystal, and is charged by desorption of Li from the layer structure. For this reason, the service capacity of a cell is determined by the quantity of Li which carries out ejection and insertion. Although it can consider that the layer structure of $LiCoO_2$ is what Li becomes a pillar and supports between the layers of CoO_2, Even if it is discharged after that and inserts Li, the lithium secondary battery using the conventional $LiCoO_2$ tends to produce an unrestorable defect in the layer structure, in order to take the unstable state of the pillar slack Li ****ing and being easy to transform the layer structure in the case of charge. For this reason, if the lithium secondary battery using $LiCoO_2$ passes through a charging and discharging cycle, service capacity will fall easily gradually, and as a result, the cycle characteristic became low easily. Since the ejection and insertion of Li are performed from the surface of a $LiCoO_2$ crystal, the diffusion rate to the crystal surface of Li in the layer structure is one factor which determines a rate characteristic. Collapse arises in the layer structure, the lithium secondary battery using the conventional $LiCoO_2$ is seen in it, the diffusion rate of upper Li falls, and the rate characteristic fell easily. Since more Li(s) would be extracted rather than the case of the low voltage and the layer structure of $LiCoO_2$ would collapse easilier if it charges by high tension, it was difficult for the lithium secondary battery using the conventional $LiCoO_2$ to repeat charge and discharge reversibly by high tension.

[0050]Since the lithium cobalt system multiple oxide concerning this invention is a specific thing which is expressed with the above-mentioned general formula (1), even if the ejection and insertion of Li are performed as positive active material of a lithium secondary battery, collapse of the layer structure, etc. do not take place easily. Therefore, the lithium secondary battery concerning this invention has few falls of the discharge voltage of battery capacity, especially the discharge last stage, they are excellent in a rate characteristic, and even if it is under the high tension not more than 4.5V, it turns into a lithium secondary battery with little cycle degradation.

[0051]The lithium secondary battery concerning this invention, for example A notebook computer, a laptop computer, It is used for consumer electronics, such as electronic equipment, such as a pocket word processor, a cellular phone, a cordless phone unit, a portable CD player, radio, a liquid crystal television, a backup power supply, an electric shaver, memory card, and a video movie, a car, an electric motor, and a game machine machine.

[0052]

[Example]Hereafter, although an example explains this invention in detail, this invention is not limited to these.

[0053]Weighing of example $1Co_3O_4$(mean particle diameter of 2 micrometers)41g, $Li_2CO_3$19.0g, and (mean particle diameter of 3 micrometers) the ZrO_2(mean particle diameter of 1 micrometer)0.06g was carried out, it fully mixed by dry type, and the mixture was obtained. The mole ratio of Li in this mixture, etc. are shown in Table 1. Next, this mixture was calcinated at 1000 ** for 5 hours. The lithium cobalt system multiple oxide which grinds and classifies the obtained fired material and is expressed with $Li_{1.001}Co_{0.999}Zr_{0.001}O_{2.001}$ was obtained. Material identification was performed with the X-ray diffraction method. The physical properties of this lithium cobalt system multiple oxide, etc. are shown in Table 2. The obtained lithium cobalt system multiple oxide was mixed at a rate of 91 % of the weight of lithium cobalt system multiple oxides, 6 % of the weight of graphite powder, and 3 % of the weight of polyvinylidene fluorides, and the anode agent was prepared. Next, N-methyl-2-pyrrolidinone was made to distribute this and the kneading paste was prepared. After applying this kneading paste to aluminum foil, it dried and pressed, pierced in a disk 15 mm in diameter, and the anode board was obtained. The lithium secondary battery was produced using each member, such as a separator, a negative electrode, an anode, a collecting electrode plate, mounting hardware, an external terminal, and an electrolysis solution, using this anode board. Among these, the negative electrode used for the electrolysis solution what dissolved $LiPF_6$1 mol in 1 l. of 1:1 kneading liquid of ethylene carbonate and methylethyl carbonate using metal lithium foil. By operating the produced lithium secondary battery at a room temperature, changing a discharge rate, and performing charge and discharge, service capacity was measured and the degree, rate characteristic, and cycle characteristic of the fall of discharge voltage of the discharge last stage were investigated. The average operating potential of 90 to 100% of the depth of discharge in a rate characteristic examination compared the degree of the fall of the discharge voltage of the discharge last stage. The result of a rate characteristic is shown in Table 3 and 4, and the result of a cycle characteristic is shown in Table 5. These measuring methods are shown below. The discharge characteristic of 1 cycle eye of the discharge rate [in / for the discharge characteristic of 1 cycle eye of the discharge rate 0.2C in a rate characteristic examination / drawing 4 and a high-tension cycle characteristic examination] 0.2C is shown in

drawing 5.

[0054]- After charging to 4.3V over 5 hours to rate (Rate) characteristic test **** and an anode by 1.0C by constant current voltage (CCCV) charge, the charge and discharge made to discharge to 2.7V with the discharge rate 0.2C were performed, and service capacity was measured for every cycle by making these operations into one cycle. The arithmetic mean of each service capacity of 3 cycle repetition, 1 cycle eye - 3 cycle eye was calculated, and this cycle was made into service capacity [in / for this value / 0.2C]. The above-mentioned operation was performed respectively similarly with the discharge rates 0.5C, 1C, and 2C, and the service capacity in each discharge rate was calculated. It is shown that it is shown that the one where the rate characteristic of the ratio of the service capacity of 2C to the service capacity of 0.2C is large in Table 3, and the service capacity in 0.2C is larger is excellent, and the one where the average operating potential between 90 to 100% of depth of discharge is higher is excellent in Table 4.

[0055]- After charging to 4.45V over 5 hours to high-tension cycle characteristic examination **** and an anode by 1.0C by constant current voltage (CCCV) charge, the charge and discharge made to discharge to 2.7V with the discharge rate 0.2C were performed, and service capacity was measured for every cycle by making these operations into one cycle. The capacity maintenance rate was computed for this cycle with the following formula from each service capacity of 20 cycle repetition, 1 cycle eye, and 20 cycle eye. Service capacity of 1 cycle eye was made into initial service capacity.

[0056]

[Equation 1]Capacity maintenance rate (%) =(service capacity of service capacity / 1 cycle eye of 20 cycle eye) x100 [0057]

[Table 1]

	混合物中のモル数(mol)			Zr化合物の平均粒子径(μm)	M_{Li}／(M_{Co}+M_{Zr}+M_{Me})	M_{Zr}／M_{Co}
	M_{Li}	M_{Co}	M_{Zr} (×10^{-4})			
実施例1	0.514	0.511	4.87	1	1.005	0.001
実施例2	0.517	0.511	9.74	1	1.010	0.002
実施例3	0.520	0.511	25.2	1	1.013	0.005
実施例4	0.514	0.511	4.92	1	1.005	0.001
比較例1	0.514	0.511	−	−	1.005	−
比較例2	0.536	0.586	58.4	1	0.906	0.01
比較例3	0.514	0.511	106	1	1.028	0.02
比較例4	0.514	0.511	304	1	0.949	0.06

* M_{Li}, M_{Co}, M_{Zr}, and M_{Me} show the number of mols of Li, Co, Zr, and Me among front, respectively.
[0058]
[Table 2]

	焼成後に得られた物質	平均粒子径（μm）	BET比表面積（m²/g）
実施例1	$Li_{1.001}Co_{0.999}Zr_{0.001}O_{2.001}$	6.5	0.39
実施例2	$Li_{1.002}Co_{0.998}Zr_{0.002}O_{2.002}$	7.2	0.35
実施例3	$Li_{1.005}Co_{0.995}Zr_{0.005}O_{2.005}$	6.9	0.36
実施例4	$Li_{1.001}Co_{0.999}Zr_{0.001}O_{2.001}$	6.8	0.36
比較例1	$LiCoO_2$	7.3	0.38
比較例2	混合物A*1	6.2	0.42
比較例3	混合物B*2	4.8	0.53
比較例4	混合物C*3	5.1	0.49

*1 Mixture *2 of mixture A:Zr substitution $LiCoO_2$, unreacted ZrO_2, and unreacted Co_3O_4 Mixture B:Zr substitution $LiCoO_2$, Mixture *3 of $LiZrO_3$ and unreacted ZrO_2 Mixture of mixture C:Zr substitution $LiCoO_2$, unreacted ZrO_2, and unreacted Co_3O_4[0059]
[Table 3]

	放電容量(mAH/g)				放電容量の比
	0.2C	0.5C	1C	2C	2C/0.2C
実施例1	161.3	158.1	148.6	129.3	80.2 %
実施例2	161.5	157.6	150.2	131.5	81.4 %
実施例3	160.3	155.3	147.1	132.6	82.7 %
実施例4	161.2	157.9	150.4	130.3	80.8 %
比較例1	162.1	158.5	150.2	113.7	70.1 %
比較例2	149.8	145.3	121.5	100.9	67.4 %
比較例3	147.5	143.1	121.1	99.8	67.7 %
比較例4	141.3	139.2	122.3	97.5	69.0 %

[0060]
[Table 4]

	放電深度９０～１００％の間の平均作動電圧（V）			
	0.2C	0.5C	1C	2C
実施例１	3.76	3.68	3.55	3.43
実施例２	3.76	3.68	3.54	3.44
実施例３	3.77	3.69	3.56	3.45
実施例４	3.76	3.68	3.53	3.45
比較例１	3.75	3.62	3.30	2.90
比較例２	3.75	3.64	3.35	3.11
比較例３	3.74	3.65	3.49	3.20
比較例４	4.74	3.64	3.48	3.18

[0061]
[Table 5]

	初期放電容量 (mAH/g)	容量維持率 （%）
実施例１	185.6	94.1
実施例２	182.4	95.4
実施例３	182.1	96.1
実施例４	184.7	94.3
比較例１	177.3	51.8
比較例２	163.3	86.2
比較例３	161.1	88.5
比較例４	158.2	89.1

[0062]Weighing of example $2Co_3O_4$(mean particle diameter of 2 micrometers)41g, Li_2CO_3 (mean particle diameter of 3 micrometers)19.1g, and the ZrO_2(mean particle diameter of 1 micrometer)0.12g was carried out, it fully mixed by dry type, and the mixture was obtained. The mole ratio of Li in this mixture, etc. are shown in Table 1. Next, this mixture was calcinated at 1000 ** for 5 hours. The lithium cobalt system multiple oxide which grinds and classifies the obtained fired material and is expressed with $Li_{1.002}Co_{0.998}Zr_{0.002}O_{2.002}$ was obtained. Material identification was performed like Example 1. The physical properties of this lithium cobalt system multiple oxide, etc. are shown in Table 2. The lithium secondary battery was produced for the obtained lithium cobalt system multiple oxide like Example 1, and the degree,

rate characteristic, and cycle characteristic of the fall of discharge voltage of the discharge last stage were investigated. The result of a rate characteristic is shown in Table 3 and 4, and the result of a cycle characteristic is shown in Table 5.

[0063]Weighing of o_3O_4(mean particle diameter of 2 micrometers) 41 g of example 3C, Li_2CO_3 (mean particle diameter of 3 micrometers)19.2g, and the ZrO_2(mean particle diameter of 1 micrometer)0.31g was carried out, it fully mixed by dry type, and the mixture was obtained. The mole ratio of Li in this mixture, etc. are shown in Table 1. Next, this mixture was calcinated at 1000 ** for 5 hours. The lithium cobalt system multiple oxide which grinds and classifies the obtained fired material and is expressed with $Li_{1.005}Co_{0.995}Zr_{0.005}O_{2.005}$ was obtained. Material identification was performed like Example 1. The physical properties of this lithium cobalt system multiple oxide, etc. are shown in Table 2. The X diffraction figure of this lithium cobalt system multiple oxide is shown in drawing 1. The lithium secondary battery was produced for the obtained lithium cobalt system multiple oxide like Example 1, and the degree, rate characteristic, and cycle characteristic of the fall of discharge voltage of the discharge last stage were investigated. The result of a rate characteristic is shown in Table 3 and 4, and the result of a cycle characteristic is shown in Table 5.

[0064]Weighing of example $4Co_3O_4$(mean particle diameter of 2 micrometers)41g, Li_2CO_3 (mean particle diameter of 3 micrometers)19.0g, and 0.24 g of the zirconium acetylacetonato ($Zr(CH_3COCHCOCH_3)_4$) (mean particle diameter of 1 micrometer) is carried out, It fully mixed by dry type and the mixture was obtained. The mole ratio of Li in this mixture, etc. are shown in Table 1. Next, this mixture was calcinated at 1000 ** for 5 hours. The lithium cobalt system multiple oxide which grinds and classifies the obtained fired material and is expressed with $Li_{1.001}Co_{0.999}Zr_{0.001}O_{2.001}$ was obtained. Material identification was performed like Example 1. The physical properties of this lithium cobalt system multiple oxide, etc. are shown in Table 2. The lithium secondary battery was produced for the obtained lithium cobalt system multiple oxide like Example 1, and the degree, rate characteristic, and cycle characteristic of the fall of discharge voltage of the discharge last stage were investigated. The result of a rate characteristic is shown in Table 3 and 4, and the result of a cycle characteristic is shown in Table 5.

[0065]Weighing of comparative example $1Co_3O_4$(mean particle diameter of 2 micrometers)41g and the Li_2CO_3(mean particle diameter of 3 micrometers)19g was carried out, it fully mixed by dry type, and the mixture was obtained. The mole ratio of Li in this mixture, etc. are shown in Table 1. Next, this mixture was calcinated at 1000 ** for 5 hours. The obtained fired material was ground and classified and $LiCoO_2$ was obtained. Material identification was performed like

Example 1. The physical properties of this $LiCoO_2$, etc. are shown in Table 2. The lithium secondary battery was produced for the obtained lithium cobalt system multiple oxide like Example 1, and the degree, rate characteristic, and cycle characteristic of the fall of discharge voltage of the discharge last stage were investigated. The result of a rate characteristic is shown in Table 3 and 4, and the result of a cycle characteristic is shown in Table 5. The discharge characteristic of 1 cycle eye of the discharge rate [in / for the discharge characteristic of 1 cycle eye of the discharge rate 0.2C in a rate characteristic examination / drawing 4 and a high-tension cycle characteristic examination] 0.2C is shown in drawing 5.
[0066]Weighing of comparative example $2Co_3O_4$(mean particle diameter of 2 micrometers) 47g, Li_2CO_3(mean particle diameter of 3 micrometers)19.8g, and the ZrO_2(mean particle diameter of 1 micrometer)0.72g was carried out, it fully mixed by dry type, and the mixture was obtained. The mole ratio of Li in this mixture, etc. are shown in Table 1. Next, this mixture was calcinated at 1000 ** for 5 hours. The obtained fired material was ground and classified and the mixture (mixture A) of Zr substitution $LiCoO_2$, unreacted ZrO_2, and unreacted Co_3O_4 was obtained. Material identification was performed like Example 1. The physical properties of the mixture A, etc. are shown in Table 2. 2 theta which originates in ZrO_2 by Cu-K alpha rays with an X-ray diffraction method = when it asked for the diffraction intensity of about 28 degrees and the ullage of ZrO_2 was measured with the absolute calibration method, ZrO_2 was 1.7 % of the weight. The X diffraction figure of the mixture A is shown in drawing 2. Inside of drawing 2, 2 theta = the peak to which about 37 degrees [28 degrees, 31 degrees, and] ** was given shows the peak of ZrO_2. The lithium secondary battery was produced for the mixture A like Example 1, and the degree, rate characteristic, and cycle characteristic of the fall of discharge voltage of the discharge last stage were investigated. The result of a rate characteristic is shown in Table 3 and 4, and the result of a cycle characteristic is shown in Table 5.
[0067]Weighing of o_3O_4(mean particle diameter of 2 micrometers) 41 g of comparative example 3C, Li_2CO_3(mean particle diameter of 3 micrometers)19.8g, and the ZrO_2(mean particle diameter of 1 micrometer)1.31g was carried out, it fully mixed by dry type, and the mixture was obtained. The mole ratio of Li in this mixture, etc. are shown in Table 1. Next, this mixture was calcinated at 1000 ** for 5 hours. The obtained fired material was ground and classified and the mixture (mixture B) of Zr substitution $LiCoO_2$, $LiZrO_3$, and unreacted ZrO_2 was obtained. Material identification was performed like Example 1. The physical properties of the mixture B, etc. are shown in Table 2. When the ullage of ZrO_2 was measured like the comparative example 2, ZrO_2 was 2.5 % of the weight. The X diffraction figure of the mixture B is shown in drawing 3. Inside of drawing 3, 2 theta = the peak to which about 37 degrees [28

degrees, 31 degrees, and] ** was given shows the peak of ZrO_2. The lithium secondary battery was produced for the mixture B like Example 1, and the degree, rate characteristic, and cycle characteristic of the fall of discharge voltage of the discharge last stage were investigated. The result of a rate characteristic is shown in Table 3 and 4, and the result of a cycle characteristic is shown in Table 5.

[0068]Weighing of comparative example $4Co_3O_4$(mean particle diameter of 2 micrometers) 41g, Li_2CO_3(mean particle diameter of 3 micrometers)19g, and the ZrO_2(mean particle diameter of 1 micrometer)3.75g was carried out, it fully mixed by dry type, and the mixture was obtained. The mole ratio of Li in this mixture, etc. are shown in Table 1. Next, this mixture was calcinated at 1000 ** for 5 hours. The obtained fired material was ground and classified and the mixture (mixture C) of Zr substitution $LiCoO_2$, unreacted ZrO_2, and unreacted Co_3O_4 was obtained. Material identification was performed like Example 1. The physical properties of the mixture C, etc. are shown in Table 2. When the ullage of ZrO_2 was measured like the comparative example 2, ZrO_2 was 7.1 % of the weight. The lithium secondary battery was produced for the mixture C like Example 1, and the degree, rate characteristic, and cycle characteristic of the fall of discharge voltage of the discharge last stage were investigated. The result of a rate characteristic is shown in Table 3 and 4, and the result of a cycle characteristic is shown in Table 5.

[0069]The result of Table 3 - 5 shows that the lithium cobalt system multiple oxide obtained in Examples 1-4 is excellent in the charge-discharge cycle characteristic under high tension. Since Zr atom dissolves uniformly to $LiCoO_2$ and ZrO_2 does not remain, this is conjectured to be because it to prevent the layer structure of $LiCoO_2$ collapsing when Li is drawn out. On the other hand, the comparative examples 1-4 have the low service capacity per weight, and it turns out that the rate characteristic and the cycle characteristic are seldom improved. Since ZrO_2 of that to which Zr atom is dissolving uniformly to $LiCoO_2$ remains, this is conjectured that only the quantity of residual ZrO_2 is because the service capacity per weight is falling. The result of drawing 4 shows that the shoulder which made the zirconium compound the discharge curve last stage clearly compared with the thing of the additive-free comparative example 1 is seen, and the lithium cobalt system multiple oxide of Example 1 is maintaining high tension to the last of discharge.

[0070]

[Effect of the Invention]The lithium cobalt system multiple oxide concerning this invention is a lithium cobalt system multiple oxide in which the zirconium atom dissolved uniformly to the inside of lithium cobalt system compound oxide particles.

If this lithium cobalt system multiple oxide is used as positive active material of a lithium secondary battery, the fall of the discharge voltage of the discharge last stage is small, and excellent in a rate characteristic, and even if it repeats charge and discharge under high tension, a lithium secondary battery with little degradation of a cycle characteristic will be obtained further.

[Translation done.]